Table 1. *Observed and calculated intensities from both neutron and X-ray diffraction patterns of* Mn_2Au

I, normalized to 100 for the most intense reflexion in each case.

Reflexion	Neutron I_{calc}	Neutron I_{obs}	X-ray I_{calc}	X-ray I_{obs}
002	47	78	16	16
101	100	100	29	45
110	0	0	63	80
103	0	0	100	100
004	12	18	3	4
112	45	38	10	18
200	0	0	22	22
114	27	18	5	11
202	26	15	4	5
105	25	17	4	9
211	47	28	7	16
006	0	0	6	7
213	0	10	37	47
204	19		3	

lian Atomic Energy Commission. One of us (P.W.) held a Commonwealth Postgraduate Scholarship.

References

GAUNT, P. & EDEN, A. (1965). *Acta Cryst.* **19**, 476.
HALL, E. O. & ROYAN, J. (1959). *Acta Cryst.* **12**, 607.
RAUB, E., ZWICKER, U. & BAUR, H. (1953). *Z. Metallk.* 44, 312.

Acta Cryst. (1970). A **26**, 381

A note on the greatest value of the Bijvoet ratio. By A. K. SINGH, *Materials Science Division, National Aeronautical Laboratory, Bangalore-17, India*

(*Received* 12 *June* 1969)

The greatest value of the Bijvoet ratio $\Delta I/I$, has been studied as a function of I. It is shown that the maximum value of $\Delta I/I$ is 2 which occurs only when $I \le I_c$; $I_c = 2\delta(\Sigma f_A)^2$ if $\Sigma f_A \langle \Sigma f_N \rangle \sqrt{1+\delta^2}\Sigma f_A$, otherwise $I_c = 2\delta^2/(1+\delta^2)\,(\Sigma f_N)^2$ (f_N is the scattering factor of the normal scatterers and f_A the real part of scattering factor of the anomalous scatterers); $\delta = \Delta f''/f_A$. For $I > I_c$, the greatest value decreases approximately as the inverse of I and rapidly approaches zero as the maximum possible value of I is reached.

For comparison with theory of the observed anomalous dispersion data from a non-centrosymmetric structure, it is convenient to use a quantity $\Delta I/I = |[|F(H)|^2 - |F(\bar{H})|^2]|/[|F(H)|^2 + |F(\bar{H})|^2]$ (H and $\bar{H}$ indicate indices hkl and $\bar{h}\bar{k}\bar{l}$) as a measure of the anomalous dispersion effect exhibited by a Crystal (Lachariasen, 1965). In the present communication the greatest value of $\Delta I/I$ as a function of I has been studied. This analysis is of interest because it makes possible the calculation of the upper limits of $\Delta I/I$ in a given structure. It must he emphasized that these limits are inherent in the function $\Delta I/I$. Though there is no assumption in the theory, its practical application does require a knowledge of the scattering factors of the atoms in the crystal. Any uncertainty in the Scattering factors will lead to some practical difficulties which are discussed of the end at this paper.

Maximum of $\Delta I/I$

Let us consider a noncentrosymrnetric structure with n_A identical anomalous scatterers having a scattering factor of the form $(f_{0A} + \Delta f'_A + i\Delta f''_A)$ and n_N normal scatterers. It can be easily shown that

$$\Delta I/I = |[|F(H)|^2 - |F(\bar{H})|^2]|/\tfrac{1}{2}[|F(H)|^2 + |F(\bar{H})|^2]$$
$$= 4k'\delta \sin\varphi(1 + \delta^2 + k'^2 + 2k'\cos\varphi)\,. \qquad (1)$$

where $k' = |F_N(H)|/|F_A(H)|$, $|F_N(H)|$ is the contribution to the structure factor from the normal scatterers while $|F_A(H)|$ is due to the real part of the scattering by the anomalous scatterers, $\delta = \Delta f''_A/(f_{0A} + \Delta f'_A)$. φ is the angle between vectors $\mathbf{F}_N(H)$ and $\mathbf{F}_A(H)$ in the complex plane. For convenience $|F_N(H)|$ and $|F_A(H)|$ will be denoted by x and y. The limits of x and y are $0 \le x \le x_{max}$ and $0 \le y \le y_{max}$ where $x_{max} = \sum_1^{n_N} f_i$ and $y_{max} = n_A(f_{A0} + \Delta f'_A)$. Further $0 \le \varphi \le \pi$.

By definition it is obvious that the maximum value of $(\Delta I/I)$ is 2 and that it occurs when $|F(\bar{H})|^2 = 0$. The following analysis provides additional information. Considering $(\Delta I/I)$ as a function of two variables k' and φ [equation (1)], it can be easily shown that maximum occurs when $k' = \sqrt{1+\delta^2}$. Since δ is in general small, $k' \simeq 1$ and $\varphi \simeq \pi$. For these values of k' and φ it can bc shown that

$$|F(H)|^2 = 4\delta^2|F_A(H)|^2$$

and $|F(\bar{H})|^2 = 0$.

From this, it can be easily deduced that I_c, the maximum value of I *for which* $\Delta I/I = 2$ can occur, is given by

$$I_c = 2\delta^2 y_{max}^2\,,$$

if $y_{max} < x_{max} > \sqrt{1+\delta^2}\,y_{max}$, and

$$I_c = 2\delta^2 x_{max}^2/(1+\delta^2)$$

if $x_{max} \le y_{max}$ *or* $y_{max} < x_{max} \le \sqrt{1+\delta^2}\,y_{max}$

It is seen that I_c is small compared with the average value of I.

Greatest value of $\Delta I/I$

For $I > I_c$, $(\Delta I/I)$ does not possess a maximum and in this we shall investigate the greatest value taken by $(\Delta I/I)$ when x, y and φ are varied continuously over the entire range of permissible values such that

$$I = \tfrac{1}{2}[|F(H)|^2 + |F(\bar{H})|^2] = (1+\delta^2)y^2 + x^2 + 2xy\cos\varphi$$

is a chosen constant.

Let us first consider the case $y_{max} < x_{max} > \sqrt{1+\delta^2}\,y_{max}$. The reason for considering this condition will become clear later. (1) can be rewritten as follows:

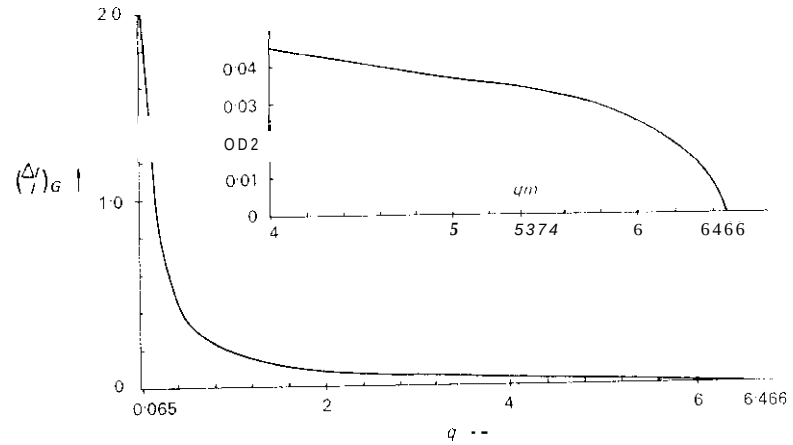

Fig. 1. Plot of $(\Delta I/I)_G$ as a function of q Sol L-tyrosine hydrochloride. Radiation. Cu $K\alpha$: sin $\theta/\lambda = 0.1$

$$\Delta I/I = 4\delta k' \sin\varphi/q'^2 \qquad (2)$$

where

$$q' = 1/y^2 = 1 + \delta^2 + k'^2 + 2k' \cos\varphi \ .$$

For a fixed value of q', $\Delta I/I$ attains a maximum value

$$(\Delta I/I)_{\max} = \frac{4\delta}{q'^2}[q'^2 - \delta^2]^{1/2} \qquad (3)$$

and occurs when

$$q'^2 + 2 = (1 + \delta^2 + k'^2) \qquad (4a)$$

and

$$\cos\varphi = -1/k' \ . \qquad (4b)$$

Next, considering the variation in q', it can be shown that the greatest value of $\Delta I/I$ for a given I occurs when $y = y_{\max}$. Thus

$$\left(\frac{\Delta I}{I}\right)_G = \frac{4\delta}{q^2}[q^2 - \delta^2]^{1/2}, \qquad (5)$$

where $q = 1/y^2_{\max}$. Equation (5) is valid in the range $2\delta^2 \le q^2 \le q_m^2$ where $q_m^2 = k_m^2 + \delta^2 - 1)$, $k_m = x_{\max}/y_{\max}$. From (4b) it is clear that $k > 1$ and this is possible only if $y_{\max} < x_{\max}$, a condition assumed at the outset. $(\Delta I/I)_G = 2$ occurs when $q^2 = 2\delta^2$, *i.e.* $k^2 = 1 + \delta^2$. This requires the condition $x_{\max} > \sqrt{(1+\delta^2)}\, y_{\max}$.

For $q_m^2 \le q^2 \le q^2_{\max}$, the greatest value is given by

$$\left(\frac{\Delta I}{I}\right)_G = \frac{4\delta}{q^2} k_m \sin\varphi' \qquad (6a)$$

where

$$\varphi' = \cos^{-1}[q^2 - (1 + \delta^2 + k_m^2)]/2k_m \qquad (6b)$$

Similar arguments can be extended easily to the cases

$$y_{\max} < x_{\max} \le \sqrt{1 + \delta^2}\, y_{\max} \text{ and } x_{\max} \ge y_{\max}.$$

For illustration, numerical calculations have been made for L-tyrosine hydrochloride. Fig. 1 shows a plot of $(\Delta I/I)_G$ as a function of q. An isotropic temperature factor ($B = 3.0$ Å^2, Srinivasan, 1959) has been used for all the atoms for calculating $x_{\max}$ and $y_{\max}$. The scattering factors for various atoms have been taken from Cromer & Waber (1965) and $\Delta f' = -0.33$ and $\Delta f'' = 0.72$ for Cl for Cu $K\alpha$ (Cromer, 1965). The quantities $x_{\max}$, $y_{\max}$, δ and q depend on the Bragg angle. Fig. 1 has been drawn for sin $\theta/\lambda = 0.1$.

For $q \le q_c$ ($q_c = 0.065$), $(\Delta I/I)_{\max} = 2$. For $q_c \le q \le q_m$ ($q_m = 5.374$), $(\Delta I/I)_G$ drops steeply according to (5) and for $q_m \le q \le q_{\max}$ ($q_{\max} = 6.466$), $(\Delta I/I)_G$ varies according to (6).

In order to see how close the observed values of $(\Delta I/I)$ (Partliasarathy, 1962) are to the corresponding values of $(\Delta I/I)_G$, calculations have been done for a few reflexions and the results are shown in Table 1. It is seen that in certain cases $(\Delta I/I)_{\rm obs}$ are close to $(\Delta I/I)_G$. In no case should $(\Delta I/I)_{\rm obs}$ exceed $(\Delta I/I)_G$. However, in practice $(\Delta I/I)_{\rm obs} > (\Delta I/I)_G$ may be encountered due to errors in the measurement of intensities and to errors in scale and temperature factors. For reflexion 680, $(\Delta I/I)_{\rm obs}$ is slightly more than $(\Delta I/I)_G$, the difference being only 1·3 per cent. This can be explained on the basis of errors in measurement and the errors in scale and temperature factors.

Table 1. *A comparison of* $(\Delta I/I)_{\rm obs}$ *with corresponding* $(\Delta I/I)_G$ *for* L-*tyrosene hydrochloride*

hkl	$(\Delta I/I)_{\rm obs}$	$(\Delta I/I)_G$	*hkl*	$(\Delta I/I)_{\rm obs}$	$(\Delta I/I)_G$
0 2 0	0·169	0·213	2 5 0	0·174	0·533
2 2 0	0·178	0·620	2 6 0	0·164	0·395
1 1 0	0·051	0·149	4 6 4	0·238	0·525
4 2 0	0·116	0·430	5 6 0	0·209	0·656
5 2 0	0·142	0·541	6 6 0	0·123	0·497
1 3 0	0·133	0·394	9 6 0	0·250	0·612
5 3 0	0·184	0·535	1 7 0	0·209	0·916
9 3 0	0·339	0·455	2 7 0	0·243	0·453
1 4 0	0·186	0·295	3 7 0	0·210	0·259
4 4 0	0406	1·200	2 8 0	0·225	0·538
10 4 0	0·091	0·266	6 8 0	0·353	0·348
1 5 0	0·128	0·467	1 9 0	0·593	0·937

The author wishes to thank Dr S. Ramaseshan for his keen interest in the work, Dr K. S. Viswanathan for reading the manuscript and Dr S. R. Valluri, the Director, National Aeronautical Laboratory, for his continued encouragement.

References

CROMER, D. T. (1965). *Acta Cryst.* **18**, 17.
CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104.
PARTHASARATHY, R. (1962). *Acta Cryst.* **15**, 41.
SRINIVASAN, R. (1959). *Proc. Indian Acad. Sci.* A **50** (1), 19.
ZACHARIASEN, W. H. (1965). *Acta Cryst.* **18**, 714.